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OF
DICOMA ANOMALA

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The small plant, *Dicoma anomala*, Sond., belonging to the *Compositae*, is known in South Africa by the Kaffir name of *in-nyongwane*. It is reputed to possess medicinal value, the powdered root being administered for colic, but it is also used for a very singular purpose. If a Kaffir goes to a strange place, he chews a little of the root, in the belief that, if he then eat any poisoned food, he will immediately vomit it (Smith, 'A Contribution to South African Materia Medica,' Cape Town, 1895, p. 64).

Dicoma anomala is plentiful at Main, in Tembuland, and on the stony hills in the midlands of Natal (Wood, *Trans. South African Phil. Soc.*, 1908, 18, II., 184). Its leaves possess an intensely bitter taste.

No information has hitherto been obtained regarding the constituents of *Dicoma anomala*. A summary of the results of the present investigation will be found at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation consisted of the entire, air-dried plant of *Dicoma anomala*, Sond., which had been specially collected for the purpose in South Africa. The greater part of the material was represented by the thick, woody roots, the leaves and stems being thin and small.

Test for an Alkaloid.—A quantity (10 grammes) of the ground material was digested with Prollius fluid, and the resulting extract subjected to the usual tests for an alkaloid, when indications of the presence of a small amount of such a substance were obtained.

Preliminary Extraction of the Plant.—A quantity (20 grammes) of the crushed material was extracted successively in a Soxhlet apparatus with various solvents, when

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the following amounts of extract, dried at 120° , were obtained :—

Petroleum (b.p. $35-50^{\circ}$) extracted	0.15 Gm.	=	0.75 per cent.
Ether	0.62 „	=	3.10 „ „
Chloroform	0.19 „	=	0.95 „ „
Ethyl Acetate	1.29 „	=	6.45 „ „
Alcohol	0.80 „	=	4.30 „ „

Total = 2.11Gms. = 10.55 per cent.

For the purpose of a complete examination, a quantity (21.97 kilogrammes) of the ground material was thoroughly extracted with hot alcohol, when, after the removal of the greater part of the solvent, 4.643 kilogrammes of a dark-coloured extract were obtained.

The entire amount of the above-mentioned extract was mixed with water, and steam passed through the mixture for several hours, when a quantity (1.5 grammes) of an essential oil was removed. This oil, distilled from $130-200^{\circ}$ under the ordinary pressure, and was a pale yellow liquid, possessing a pungent odour.

After the distillation of the extract with steam, as above described, there remained in the distillation flask a dark-coloured, aqueous liquid (A) and a dark brown resin (B). The latter was separated, and thoroughly washed with water, the washings being concentrated and added to the main bulk of the aqueous liquid.

EXAMINATION OF THE AQUEOUS LIQUID (A).

The aqueous liquid (A) was first repeatedly extracted with ether, and subsequently with chloroform, but only small amounts of dark red amorphous material were removed by this treatment. The aqueous liquid was then extracted many times with warm amyl alcohol, the resulting extracts being concentrated to a small bulk under diminished pressure, when a large amount of yellow, amorphous matter separated. The latter was collected on a filter, and washed, but it was extremely hygroscopic, and rapidly became converted into a brown, viscid mass. The filtrate was largely diluted with ether, and filtered, when a further quantity of a similar deliquescent product was obtained. The ether was removed from the filtrate, and the latter concentrated, when the material remaining dissolved in the amyl alcohol was precipitated by means of chloroform. A brown, granular solid was thus obtained, which yielded a green colour with ferric chloride, but nothing definite could be obtained from it.

ISOLATION OF 3:4-DIHYDROXYCINNAMIC ACID.

The above-mentioned deliquescent product was found to contain nothing of a glucosidic nature, and it could not be crystallised. A portion of it was heated for a short time with 5 per cent. aqueous potassium hydroxide, after which

the mixture was acidified and extracted many times with ether. The ethereal liquid was extracted successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide. The liquids obtained by means of the last-mentioned two alkalis, on acidification, yielded nothing definite, but on acidifying the ammonium carbonate extract and extracting the liquid with ether a quantity of a crystalline solid was obtained. The latter, after recrystallisation from dilute alcohol, yielded small, brownish-coloured prisms, melting and decomposing at 217° . This substance yielded the catechol reaction when treated with ferric chloride, and was identified as 3:4-dihydroxycinnamic acid (Found, C = 60.3; H = 4.6. Calc., C = 60.0; H = 4.4 per cent.). Its identity was further confirmed by the mixed melting point test, employing an authentic specimen of the above-mentioned acid.

The aqueous liquid which had been extracted with amyl alcohol was deprived of the latter by distillation with steam, and treated with a slight excess of basic lead acetate solution, when a bulky, yellow precipitate was produced. The latter was collected, washed, suspended in water, and decomposed by means of hydrogen sulphide. The filtered liquid was then concentrated to a small bulk, when a brown product was obtained, but nothing definite could be isolated from it.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the lead, and, after filtering, was concentrated under diminished pressure to the consistency of a syrup. The latter evidently contained a quantity of sugar, since it readily yielded *d*-phenylglucosazone, melting at 218° .

ISOLATION OF A GLUCOSIDE.

The above-mentioned syrup containing sugar was mixed with alcohol, and the mixture kept for several days. A small amount of a colourless crystalline solid then separated, which, after recrystallisation from very dilute alcohol, melted at 243° .

0.1208 gave 0.2574 CO_2 and 0.0788 H_2O . C = 58.1; H = 7.2.
 $\text{C}_{20}\text{H}_{28}\text{O}_{17}$ requires C = 58.6; H = 7.3 per cent.

A quantity (0.2 gramme) of the substance was heated with dilute aqueous sulphuric acid for some time, and the mixture then extracted with ether. On evaporating the ethereal liquid a brownish-coloured, resinous product was obtained, which was readily soluble in most organic solvents, but could not be obtained in a crystalline condition. The acid, aqueous liquid was treated with barium hydroxide for the removal of the sulphuric acid, after which the filtered liquid was concentrated, when it was found to contain dextrose. It yielded *d*-phenylglucosazone, melting at 218° . It is thus evident that the substance melting at 243° is a glucoside, but the amount of it available did not permit of the characterisa-

tion of its hydrolytic product other than dextrose, and therefore its formula could not be definitely established. Both the glucoside and its hydrolytic product dissolved in concentrated sulphuric acid giving a deep crimson-coloured liquid, possessing a strong green fluorescence.

As it was probable that the original filtrate from the glucoside still contained some of the latter, in addition to sugar, it was heated with dilute sulphuric acid, with the endeavour to obtain more of the hydrolytic product. The material obtained, however, was small in amount and amorphous.

EXAMINATION OF THE RESIN (B).

The resin (B), which was a dark-coloured, pitch-like solid, was powdered and dried, when it amounted to 1320 grammes. It was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture successively extracted in a Soxhlet apparatus with petroleum (b.p. 35-50°), ether, chloroform, ethyl acetate, and alcohol.

PETROLEUM EXTRACT OF THE RESIN.

This extract was a dark-green, viscid mass, and amounted to 170 grammes. It was dissolved in ether, and shaken with aqueous ammonium carbonate, when a small amount of a solid product separated. The latter was collected, heated with alcoholic potassium hydroxide, the mixture deprived of a small amount of unsaponifiable matter, acidified, and the liberated acid isolated. About 0.25 gramme of a fatty acid was thus obtained, which, after crystallisation from absolute alcohol, melted at 85-86°.

0.1118 gave 0.3270 CO₂ and 0.1300 H₂O. C = 79.8; H = 12.9.

The amount of this acid was too small for further examination, but it was probably slightly impure melissic acid, which melts at 90°, and requires C=79.7; H=13.3 per cent.

The alkaline, aqueous liquid obtained on shaking the ethereal solution of the petroleum extract of the resin with ammonium carbonate, as above described, yielded only a small amount of amorphous material.

The original ethereal solution of the petroleum extract was then shaken with aqueous potassium carbonate, and subsequently washed with water. The alkaline extract and washings were acidified, when about 7 grammes of crude fatty acids were obtained. These free fatty acids were converted into their methyl esters, and the latter fractionally distilled several times under a pressure of 15 m.m. The fraction of lowest boiling-point, which distilled from 193 to 197°, yielded on hydrolysis palmitic acid, melting at 63°.

(Found, C = 75.0; H = 12.3. Calc., C = 75.0; H = 12.5 per cent.)

The remaining fractions were all small in amount, most of them being insufficient for examination. A fraction boiling at 210-215°/15 m.m., however, yielded, on hydrolysis, a small

amount of a mixture of palmitic and stearic acids, together with some unsaturated acids. The latter, which were separated from the saturated acids by means of the lead salts, were distilled, after which they gave the following results :—

0.1776 gave 0.4923 CO_2 and 0.1814 H_2O . $\text{C} = 75.6$; $\text{H} = 11.3$.
0.2234 absorbed 0.2561 iodine. Iodine value = 114.6.

A similar product subsequently obtained from the combined fatty acids, as indicated below, gave the following results :—

0.1986 gave 0.5500 CO_2 and 0.2022 H_2O . $\text{C} = 75.5$; $\text{H} = 11.3$.
0.1470 gave 0.4092 CO_2 and 0.1500 H_2O . $\text{C} = 75.7$; $\text{H} = 11.3$.
0.2282 absorbed 0.2513 iodine. Iodine value = 110.
 $\text{C}_{16}\text{H}_{30}\text{O}_2$ requires $\text{C} = 75.6$; $\text{H} = 11.8$; iodine value = 100.

It would thus appear that the unsaturated acids consisted chiefly of an acid, $\text{C}_{16}\text{H}_{30}\text{O}_2$, having one double linking, together with a small amount of an acid of a higher degree of unsaturation. An acid of the formula $\text{C}_{16}\text{H}_{30}\text{O}_2$ has been obtained by Bull (*Ber.*, 1906, 39, 3537) from cod-liver oil.

The portion of the esters of the free fatty acids of highest boiling point, which distilled from 230 to about $260^\circ/15$ m.m. yielded about 0.2 gramme of an acid, which, when crystallised from alcohol, melted at $75-78^\circ$.

0.1359 gave 0.3842 CO_2 and 0.1589 H_2O . $\text{C} = 78.9$; $\text{H} = 13.0$.
 $\text{C}_{27}\text{H}_{54}\text{O}_2$ requires $\text{C} = 79.0$; $\text{H} = 13.2$ per cent.

This substance was therefore slightly impure cerotic acid.

The original ethereal solution from which the free fatty acids had been removed by means of potassium carbonate, as above described, was shaken with aqueous potassium hydroxide. This treatment removed a small amount of a substance which exhibited the colour reactions of the anthraquinone derivatives, but the amount of it obtained was too small to permit of its characterisation.

The ethereal solution of the neutral portion of the extract was then evaporated, and the residue hydrolysed by heating with an alcoholic solution of potassium hydroxide. After the removal of the solvent the alkaline liquid was diluted with water, and deprived of unsaponifiable matter by repeated extraction with ether. The alkaline, aqueous liquid was then acidified, and the resulting acids, which amounted to about 25 grammes, isolated by means of ether. These acids were converted into the methyl ester, the latter fractionally distilled under 15 m.m. pressure, and examined in the manner already indicated in connection with the free fatty acids. This resulted in the isolation of palmitic, stearic, and arachidic acids, together with the unsaturated acids previously referred to. The stearic acid melted at $68-69^\circ$, and gave $\text{C} = 76.1$; $\text{H} = 12.6$.

($\text{C}_{18}\text{H}_{36}\text{O}_2$ requires $\text{C} = 76.1$; $\text{H} = 12.7$ per cent.)

The arachidic acid was obtained from a fraction of methyl

esters boiling at 240-250°/15 m.m., and, after crystallisation from alcohol, melted at 72-75°.

0.0940 gave 0.2654 CO₂ and 0.1075 H₂O. C = 77.0; H = 12.7.

C₂₀H₄₀O₂ requires C = 76.9; H = 12.8 per cent.

EXAMINATION OF THE UNSAPONIFIABLE MATERIAL.

The ethereal solution of the unsaponifiable material, which had been separated from the alkaline solution of the combined fatty acids, as previously described, was washed and evaporated. The residue was dissolved in absolute alcohol, when, on cooling, a sparingly soluble solid separated. The latter was collected, and washed with alcohol, after which it was found to be a mixture. It was therefore heated for some time with an excess of phthalic anhydride, the product dissolved in a mixture of chloroform and ether, and the resulting liquid shaken with aqueous sodium carbonate. A solid sodium salt of an acid phthalic ester then separated, which, when hydrolysed, yielded a small amount of a wax-like alcohol. The latter, when crystallised from a mixture of ethyl acetate and alcohol, melted at 82-83°, and appeared to be myricyl alcohol, but the amount available was too small for analysis.

The ether-chloroform mixture from which the sodium salt of the acid phthalic ester had been separated was evaporated, and the residue deprived of phthalic anhydride by heating with alcoholic potassium hydroxide, after which it was diluted with water, and extracted with ether. On evaporating the ether a solid was obtained which crystallised from ethyl acetate in nacreous leaflets, melting at 68°. (Found, C=84.8; H=14.6. Calc. for C₃₁H₆₄, C=85.3; H=14.7 per cent.) This substance was therefore the hydrocarbon hentriacontane.

ISOLATION OF A PHYSTOSTEROL, C₂₈H₄₆O.

The original alcoholic filtrate from the crude mixture of hentriacontane and myricyl alcohol was concentrated somewhat, a little water added, and the mixture kept for some time. A quantity of a solid then separated, which, when isolated, yielded the colour reactions of a phytosterol. In order to effect its purification, it was converted into the acetyl derivative, and the latter crystallised many times until it was homogeneous and of constant melting-point. It then fused at 133°.

0.1025 gave 0.3081 CO₂ and 0.1010 H₂O. C = 82.0; H = 10.9.

C₂₈H₄₅O·CO·CH₃ requires C = 81.8; H = 10.9 per cent.

The remainder of this acetyl derivative was hydrolysed with alcoholic potassium hydroxide, and the resulting phytosterol isolated. When crystallised from a mixture of dilute alcohol and ethyl acetate, it formed colourless plates, melting at 159°.

0.0976 gave 0.3011 CO₂ and 0.1010 H₂O. C=84.1; H=11.5.

C₂₈H₄₆O requires C = 84.2; H = 11.6 per cent.

It is thus seen that the above-described phytosterol differs in composition from the more commonly occurring members of this class, which possess the formula, $C_{27}H_{46}O$, and appears to be a lower homologue of stigmasterol, $C_{30}H_{50}O$.

ETHER EXTRACT OF THE RESIN.

This extract was a dark-coloured mass, amounting to 135 grammes. It was dissolved in hot alcohol, and the solution filtered, when a small amount of a sparingly soluble product was obtained. The latter was extracted in a Soxhlet apparatus, first with ethyl acetate, which removed some chlorophyll, and then with alcohol. The latter solvent slowly removed a small quantity (0.1 gramme) of a sparingly soluble substance, which, when crystallised from dilute pyridine, melted and decomposed at 260-270°, and was identified as a phytosterolin (phytosterol glucoside). On acetylation it yielded an acetyl derivative, which separated from a mixture of ethyl acetate and alcohol in colourless leaflets, melting at 150°.

The original hot alcoholic filtrate from the crude phytosterolin deposited, on cooling, a quantity (about 20 grammes) of a green-coloured solid in the form of an amorphous powder. The latter was collected, washed with cold alcohol, and dried, when it was found to melt at about 85°. It was redissolved in hot alcohol, and treated repeatedly with animal charcoal, but it could not be decolorised, nor could it be obtained in a crystalline condition. On distillation under diminished pressure, the greater portion of this amorphous product underwent decomposition, but the distillate yielded small amounts of a colourless acid melting at 82-83°, and of a neutral substance melting at 73°.

The alcoholic filtrate from the above-described amorphous material was evaporated, and the residue dissolved in ether. The ethereal solution was then shaken with dilute hydrochloric acid, when a small amount of alkaloidal material was removed. The hydrochloride of the latter was a brownish, amorphous substance, and nothing definite could be obtained from it.

The ethereal liquid from which the amorphous alkaloid had been removed was thoroughly examined, but it was found to contain only a dark green, acidic resin, from which nothing could be isolated.

CHLOROFORM, ETHYL ACETATE, AND ALCOHOL EXTRACTS OF THE RESIN.

The chloroform extract of the resin was dark brown, and amounted to 184.5 grammes. Nothing crystalline could be directly separated from it, and when its solution in chloroform was fractionally extracted with various alkalis it yielded only amorphous products. It contained nothing glucosidic, and, after heating with dilute, alcoholic potassium hydroxide, nothing crystalline could be obtained from it.

The ethyl acetate extract of the resin was a reddish-brown mass, and amounted to 346 grammes. Nothing could be

directly separated from it, and it was found to be devoid of glucosidic material. A portion of it was boiled for a few minutes with 10 per cent. aqueous potassium hydroxide, when, after acidification and extraction with ether, it yielded a quantity of 3:4-dihydroxycinnamic acid, melting at 220° . (Found, C=59.8; H=4.4. Calc., C=60.0; H=4.4 per cent.) The identity of the latter was confirmed by the preparation of its dimethyl ether (m.p. 180°) and its diacetyl derivative. The latter substance melted at 200° , a somewhat higher temperature than has previously been recorded ($191-192^{\circ}$) for the melting point of diacetyl-3:4-dihydroxycinnamic acid. (Gorter, *Annalen*, 1908, 358, 327.)

The alcohol extract of the resin was a dark brown mass, and amounted to 277.5 grammes. It contained nothing glucosidic, and no crystalline substance could be directly separated from it. On hydrolysis with alkali it yielded 3:4-dihydroxycinnamic acid.

Summary.

The material employed for this investigation consisted of the entire air-dried plant of *Dicoma anomala*, Sond., which had been specially collected in South Africa.

An alcoholic extract of the plant, when distilled in a current of steam, yielded a small amount of an essential oil. The portion of the extract which was soluble in water yielded a small amount of a colourless crystalline glucoside, which appeared to possess the formula $C_{39}H_{58}O_{17}$, and a large amount of a yellow amorphous product, which, on hydrolysis with alkali, gave 3:4-dihydroxycinnamic acid. The aqueous liquid contained, furthermore, a quantity of sugar which yielded *d*-phenylglucosazone, melting at 218° .

The portion of the extract, which was insoluble in water, formed a dark-coloured, resinous mass. It consisted largely of amorphous products, some of which gave 3:4-dihydroxycinnamic acid on hydrolysis, and a small amount of an amorphous alkaloid was also present. The following definite substances were, however, obtained from the resin: (i.) Hentriacontane, $C_{31}H_{64}$; (ii.), a phytosterol, $C_{28}H_{46}O$, which melts at 159° , and seems to be a lower homologue of stigmasterol; (iii.) palmitic, stearic, arachidic, cerotic, and melissic acids, together with some unsaturated acids which appeared to consist chiefly of a compound, $C_{16}H_{30}O_2$, such as has been obtained by Bull (*Ber.*, 1906, 39, 3537) from cod-liver oil.

